"The Spectra of Potassium, Rubidium, and Cæsium, and their Mutual Relations." By HUGH RAMAGE, B.A., St. John's College, Cambridge. Communicated by Professor G. D. LIVEING, F.R.S. Received May 14,—Read June 5, 1902.

The spectra of this group of metals have already been considered in a paper by the author, on "A Comparative Study of Spectra," &c.* It was there shown that the differences between the principal series of lines in these metals depended on the atomic mass alone; and also that there was a close connection between the subordinate series and the atomic mass. A further study of the latter series was impossible at the time of writing the paper owing to the fewness of the lines which had been observed and measured in them; practically no lines were known in the second subordinate series of rubidium and cæsium.

Some lines belonging to the subordinate series have been measured in Bunsen-flame and spark spectra by Lecoq de Boisbaudran, and in the arc spectrum by Liveing and Dewar, and by Kayser and Runge. Lehmann has measured some lines in the arc spectra in the red region. Lines recorded by these observers were found by the writer, with considerable intensity, in the oxyhydrogen flame spectra of the metals; and other lines, weaker than the above, were present which had never been recorded. Photographs of these high-temperature flame spectra were taken with a spectrometer designed by Professor Liveing, fitted with a Rowland plane grating ruled with 14,438 lines to the inch. The quartz lenses were plano-convex with a focal length for the D lines of about 778 mm. The spectra in the first and second orders were photographed, and some measurements were made in the red region by eye observations. Spark spectra were photographed, superimposed on the flame spectra, of iron and titanium principally, but other metals were also employed. These furnished the numerous fiducial lines required for the accurate determination of the wave-lengths.

The lines in the subordinate series are generally more diffuse than those in the principal series. Some of the weaker lines, notably those of cæsium, are very broad with diffuse edges; very accurate measurement of these is impossible.

Particulars of the spectra are recorded below; the oscillation frequencies are reduced to their values in a vacuum. The lines have been sorted into the principal and the first and second subordinate series, and marked P, I, or II, with the number of the line, according to Rydberg's formula, in the sixth column. The wave-lengths of the lines which have been observed before are given in the fourth column.

* 'Roy. Soc. Proc.,' vol. 70, p. 1, 1902.

In the column of observers, L. and D. represent Liveing and Dewar, K. and R., Kayser and Runge; L. de B., Lecoq de Boisbaudran.

Cæsium

Wave-length.	Oscillation frequency, in vacuum.	Intensity.	Previous measurement.	Observer.	Series and number.
6984	14314	6			
74	335	9	6973 ·9	K. and R.	I_4
6869	554	2			
29	639	2			
6722	873	9	6723 ·6	,,	I_4
6630	15079	2			
6590	171	8	—	—	II_4
6472	447	2			
6433	540	2			
6354	733	8	—	—	II_4
6217 ·6	16078 ·7	2			
13 ·33	89 ·7	8	6213 ·4	K. and R.	I_5
6034 ·43	16566 ·7	4	—	—	II_5
10 ·59	16632 ·4	8	6010 ·6	K. and R.	I_5
5847 ·86	17095 ·6	2			
45 ·31	102 ·7	8	5845 ·1	,,	I_6
39 ·33	120 ·2	2	—	—	II_5
5746 ·37	397 ·2	1	—	—	II_6
5664 ·14	649 ·7	7	5664 ·0	K. and R.	I_6
35 ·44	739 ·6	5	35 ·1	,,	I_7
5574 ·4	933 ·9	1	5572	L. de B.	II_7
68 ·9	951 ·6	1	—	—	II_6
03 ·1	18166 ·2	3	5501 ·9 ?	K. and R.	I_8
5466 ·1	289 ·2	4	5465 ·8	,,	I_7
14 ·4	463 ·8	1	—	—	I_9
07 ·5	487 ·3	1	—	—	II_7
5351	682	1	—	—	I_{10}
5341 ·15	717 ·0	3	5345	L. de B.	I_8
5304	848	<1	—	—	I_{11}
5256 ·96	19016 ·8	1	5257	L. de B.	I_9
5209	192	<1			
5199	228	<1	—	—	I_{10}
5154	396	<1	—	—	I_{11}
4593 ·30	21764 ·8	8	4593 ·34	K. and R.	P_2
55 ·46	945 ·6	10	55 ·44	,,	P_2
3888 ·75	25707 ·9	2	3888 ·83	,,	P_3
76 ·31	790 ·4	4	76 ·73	,,	P_3
3617 ·49	27635 ·7	<1	3617 ·08	,,	P_4
11 ·70	680 ·0	2	11 ·84	,,	P_4
3477 ·25	28750 ·3	1	—	—	P_5
3398 ·40	29417 ·3	1	—	—	P_6
48 ·72	29853 ·7	<1	—	—	P_7
3314	30166	<1	—	—	P_8
3287	30414	<1	—	—	P_9

Rubidium

Wave-length.	Oscillation frequency, in vacuum.	Intensity.	Previous measurement.	Observer.	Series and number.
			7950·46	Lehmann	P_1
7799	—	Very strong	7805·98	"	P_1
6306·8	15851·3	1			
6299·19	870·5	9	6297	L. de B.	I_4
6206·74	16106·8	8	6203	"	I_4
6160·04	228·9	5	6159	"	II_4
6071·04	466·8	4	—	—	II_4
5724·62	17463·2	8	5724·41	K. and R.	I_5
5654·16	680·9	3	5654·22	"	II_5
48·19	699·6	7	48·18	"	I_5
5579·3	918·1	2	—	—	II_5
5432·05	18403·9	6	5431·83	K. and R.	I_6
5391·3	543·0	1	—	—	II_6
63·15	640·3	5	5362·94	K. and R.	I_6
22·83	781·5	1	—	—	II_6
5260·51	19004·0	4	5259·8	K. and R.	I_7
34·6	098	1	—	—	II_7
5195·76	240·7	3	5194·8	K. and R.	I_7
65·35	354·1	2			
51·20	407·2	2	—	—	I_8
5132	480	<1	—	—	II_8
5089·5	642·5	1	—	—	I_3
76·3	693·6	1	—	—	I_9
37	847	1			
23	902	1	5021·8	K. and R.	I_{10}
17	926	<1	—	—	I_9
4983	20062	<1	—	—	I_{11}
67	127	<1			
4215·68	23714·4	9	4215·72	K. and R.	P_2
02·04	791·4	10	01·98	"	P_2
3591·86	27832·8	3	3591·74	"	P_3
87·27	868·4	4	87·23	"	P_3
3350·98	29833·5	1	3351·03	"	P_4
48·84	852·6	2	48·86	"	P_4
3229·26	30958·0	1	—	—	P_5
28·18	968·4	1	—	—	P_5

The isolated line λ 5165·35 is narrow and sharp; it differs, in these respects, from the lines in the series.

Potassium

Wave-length.	Oscillation frequency, in vacuum.	Intensity.	Previous measurement.	Observer.	Series and number.
7697	—	Very strong	7701·92	Lehmann	P_1
7664	—	,,	7668·54	,,	P_1
6939	14407	8	6938·8	K. and R.	II_3
13	462	7	11·2	,,	II_3
5832·25	17141·3	6	5832·23	,,	I_4
12·53	199·5	5	12·54	,,	I_4
02·12	230·8	7	02·01	,,	II_4
5782·74	288·1	6	5782·67	,,	II_4
5359·96	18651·8	4	5359·88	,,	I_5
43·38	709·6	2½	43·35	,,	I_5
40·17	720·9	3	40·08	,,	II_5
23·68	778·9	2	23·55	,,	II_5
5112·76	19553·1	2	5112·68	,,	I_6
5099·83	602·7	1	5099·64	,,	II_6
97·64	611·1	1½	97·75	,,	I_6
85·07	659·4	1	84·49	,,	II_6
4965·61	20132·5	1	4965·5	,,	I_7
4957	167	<1	56·8	,,	II_7
51·46	190·1	1	52·2	,,	I_7
4870	528	<1	4870·8	L. and D.	I_8
62	562	<1	63·8	,,	II_8
57	583	<1	56·8	,,	I_8
29	702	<1			
03	814	<1	4803·8	,,	I_9
01	823	<1	—	—	II_9
4798	836	<1	4796·8	L. and D.	
67	972	<1			
60	21002	<1	4759·8	,,	I_{10}
4642·35	21534·4	2	4642	H. and R.	
38·6	51·8	<1			
4047·39	24700·3	9	4047·36	K. and R.	P_2
44·33	719·0	10	44·29	,,	P_2
3447·56	28997·8	3	3447·49	,,	P_3
6·55	29006 3	4	6·49	,,	P_3
Present	—	<1	3217·76	,,	P_4
3217·36	31072·7	2	0·27	,,	P_4

Other lines, very feeble indeed, appear on the strong continuous spectrum in the region near 4642. The line λ 4642·35 was first observed in the spectrum of the Bessemer flame; Hartley and Ramage, 'Phil. Trans.,' A, vol. 196, p. 491, 1901.

Diagrams of these spectra were drawn, as described in my former paper, to scales of oscillation frequencies for abscissæ, and (1) atomic masses, (2) squares of atomic masses for ordinates. The conclusions previously deduced from the less complete data were thereby amply confirmed. There is undoubtedly a very close connection between the spectra and the atomic masses; and the lines, which connect the corresponding members of homologous doublets in diagram (2), do intersect on the line of zero atomic mass.

The two limits in each spectrum towards which the two subordinate series appeared to converge were determined by a slight modification of Rydberg's method combined with graphical methods. These were inserted in the diagrams and curves were drawn through the points. In diagram (1) the curves were turned away from each other and the points of bisection of the lines between the limits lay on a straight line; so also did the points of bisection of the lines between the two more refrangible and corresponding doublets of the second subordinate series. In diagram (2) the curves through the limits of the series, when produced, intersected on the line of zero atomic mass. This fact indicates that the difference between the two limits of the series, while not proportional to the square of the atomic mass, is a simple function of it. Rydberg, Kayser and Runge, and Rummel* have each shown that the differences between the convergence points of the subordinate series are approximately proportional to the squares of the atomic masses.

A diagram of the spectra and limits of the series was also drawn for the three metals to scales of wave-lengths and atomic masses. The more refrangible limits of the subordinate series and the more refrangible members of the second series now lay on straight lines; the change in wave-length was thus proportional to the atomic mass.

After a careful study of the facts and many computations, it was found possible to calculate the subordinate series with considerable accuracy by the following formulæ.

The first Subordinate Series.

The two convergence points (n_∞) of this series are obtained as follows: $n_\infty = 22830 - 21{\cdot}633\,\mathrm{W} \pm \frac{\mathrm{A}}{2}$, where W is atomic mass and A is the average difference between the doublets. The latter quantity, as determined from the lines which are best suited for accurate measurement, is for potassium 57·8, for rubidium 236·4, and for cæsium 547·6. These values, as shown above, are simple functions of the atomic mass; but the best method of expressing them is not yet clear. This formula gives the following values for n_∞ belonging to the doublets of the first subordinate series:—Potassium, 21953·9 and 22011·7; rubidium, 20861·8 and 21098·2; and cæsium 19677·2 and 20224·8.

When these values are substituted for n_∞ in Rydberg's formula,

$$n = n_\infty - \frac{\mathrm{N}_0}{(m+\mu)^2};$$

in which $n = 10^8\lambda^{-1}$, $\mathrm{N}_0 = 109675$, $m = 3.4.5 \ldots.$ and when we

* 'Proc. Roy. Soc. Victoria,' vols. 9 and 10, 1897.

also substitute for μ (assuming it to have a constant value for the series) the value

$$\mu = 0\cdot7869 - 1466\ W^2 \times 10^{-8},$$

we obtain the following results:—

Potassium

m.	Oscillation frequencies.		Differences.
	Observed.	Calculated.	
3	—	14214 ·6	
4	17141 ·3	17122 ·4	−18 ·9
5	18651 ·8	18653 ·3	+ 1 ·5
6	19553 ·1	19557 ·1	+ 4 ·0
7	20132 ·5	20134 ·7	+ 2 ·2
8	20528	20526 ·1	− 1 ·9
9	22814	20803 ·6	−10 ·4
10	21002	21007 ·4	− 5 ·4

m.	Oscillation frequencies.		Differences.
	Observed.	Calculated.	
3	—	14272 ·4	
4	17199 ·5	17180 ·2	−19 ·3
5	18709 ·6	18711 ·1	+ 1 ·5
6	19611 ·1	19614 ·9	+ 3 ·8
7	20190 ·1	20192 ·5	+ 2 ·4
8	20583	20583 ·9	+ 0 ·9
9			
10			

Rubidium

m.	Oscillation frequencies.		Differences.
	Observed.	Calculated.	
3	—	12763 ·2	
4	15870 ·5	15854 ·4	−16 ·1
5	17463 ·2	17462 ·3	− 0 ·9
6	18403 ·9	18404 ·0	+ 0 ·1
7	19004 ·0	19002 ·3	− 1 ·7
8	19407 ·2	19406 ·1	− 1 ·1
9	19693 ·6	19691 ·3	− 2 ·3
10	19902	19900 ·3	− 1 ·7
11	20062	20057 ·9	− 4 ·1

m.	Oscillation frequencies.		Differences.
	Observed.	Calculated.	
3	—	12999 ·6	
4	16106 ·8	16090 ·8	−16·0
5	17699 ·6	17698 ·7	− 0 ·9
6	18640 ·3	18640 ·4	+ 0 ·1
7	19240 ·7	19238 ·7	− 2 ·0
8	19642 ·5	19642 ·5	0
9	19926	19927 ·7	+ 1 ·7

Cæsium

m.	Oscillation frequencies.		Differences.
	Observed.	Calculated.	
3	10852 ·1	10865 ·7	+13 ·6
4	14335	14327 ·9	− 7 ·1
5	16089 ·7	16088 ·2	− 1 ·5
6	17102 ·7	17103 ·6	+ 0 ·9
7	17739 ·6	17741 ·9	+ 2 ·3
8	18166 ·2	18169 ·2	+ 3 ·0
9	18463 ·8	18469 ·1	+ 5 ·3
10	18682	18687 ·7	+ 5 ·7
11	18848	18851 ·9	+ 3 ·9

m.	Oscillation frequencies.		Differences.
	Observed.	Calculated.	
3	11404 ·1	11413 ·3	+9 ·2
4	14873	14875 ·5	+2 ·5
5	16632 ·4	16635 ·8	+3 ·4
6	17649 ·7	17651 ·2	+1 ·5
7	18289 ·2	18289 ·5	+0 ·3
8	18717 ·0	18716 ·8	−0 ·2
9	19016 ·8	19016 ·7	−0 ·1
10	19228	19235 ·3	+7 ·3
11	19396	19399 ·5	+3 ·5

The second Subordinate Series.

In this series

$$n_\infty = 22850 - 21 \cdot 812 \text{ W} \pm \frac{\text{B}}{2},$$

where B is for potassium, 57·8; for rubidium, 238·0; and for cæsium, 553·6; and

$$\mu = 0 \cdot 7990 + 7984 \text{ W}^2 \times 10^{-9}.$$

It will be observed that the doublets in the second subordinate series are more widely separated than those in the first series. It would appear also that the two series do not converge towards the same limit; the difference between the limits, however, diminishes in the different metals as the atomic mass increases. This is true on the supposition that μ is constant, and not variable as in the formula given for the principal series. Kayser and Runge hold the view that there are different limits for the two series, while both Rydberg and Rummel favour the view that the limits are the same.

The observed and calculated oscillation frequencies are as follows :—

Potassium.

m.	Oscillation frequencies.		Differences.
	Observed.	Calculated.	
3	14407	14417 ·4	+10·4
4	17230 ·8	17229 ·9	− 0 ·9
5	18720 ·9	18720 ·3	− 0 ·6
6	19602 ·7	19603 ·9	+ 1 ·2
7	20167	20170 ·5	+ 3 ·5
8	20562	20555 ·3	− 6 ·7
9	20823	20828 ·6	+ 5 ·6

m.	Oscillation frequencies.		Differences.
	Observed.	Calculated.	
3	14462	14475 ·2	+13 ·2
4	17288 ·1	17287 ·7	− 0 ·4
5	18778 ·9	18778 ·1	− 0 ·8
6	19659 ·4	19661 ·7	+ 2·3

Rubidium

m.	Oscillation frequencies.		Differences.
	Observed.	Calculated.	
3	13498	13496·7	−1·3
4	16228·9	16219·6	−9·3
5	17680·9	17671·4	−9·5
6	18543·0	18535·8	−7·2
7	19098	19091·8	−6·2
8	19480	19470·3	−9·7

m.	Oscillation frequencies.		Differences.
	Observed.	Calculated.	
3	13738	13734·7	−3·3
4	16466·8	16457·6	−9·2
5	17918·1	17909·4	−8·7
6	18781·5	18773·8	−7·7

Cæsium

m.	Oscillation frequencies.		Differences.
	Observed.	Calculated.	
3	—	12609·3	
4	15171	15180·2	+9·2
5	16566·7	16566·1	−0·6
6	17397·2	17397·3	+0·1
7	17933·9	17934·7	+0·8

m.	Oscillation frequencies.		Differences.
	Observed.	Calculated.	
3	—	13162·9	
4	15733	15733·8	+0·8
5	17120·2	17119·7	−0·5
6	17951·6	17950·9	−0·7
7	18487·3	18488·3	+1·0

The convergence points of the series as deduced in different ways are given in the following table :—

Element.	From above formulæ.			By calculation from observed lines.	From formula for principal series.*	Numbers calculated by Rydberg.
	First series.	Second series.	Mean of two series.	Mean.		
Potassium (1)	21953·9	21968·0	21960·95	21960	21969·4	21955·46
,, (2)	22011·7	22025·8	22018·75	22018	22024·3	22013·31
Rubidium (1)	20861·8	20868·3	20865·65	20865	20868·6	20869·15
,, (2)	21098·2	21106·3	21102·25	22101	21112·3	21098·83
Cæsium (1)	19677·2	19674·2	19675·7	19672	19686·7	
,, (2)	20224·8	20228·0	20226·4	20226	20234·2	

The numbers in the sixth column were obtained by the law, discovered by Rydberg and independently by Schuster, which connects the principal and subordinate series: the convergence points of the subordinate series are given by the differences between the convergence points and first lines (for which $m = 1$) of the principal series. One set of the numbers was obtained from the expression

$$\frac{N_0}{(1 + 1\cdot19126 + 0\cdot00103\,W)^2},$$

and the other set from the expression

$$\frac{N_0}{(1 + 1\cdot19126 + 0\cdot00103\,W + 182\,W^2 \times 10^{-8})^2}.$$

The figures in this column agree best with those of the second subordinate series in the third column; and it will be remarked as confirming the closer connection between the principal and second subordinate series, that the results calculated for the latter series of rubidium differ by about nine units, whereas those given by the formula for the principal series differ by about 27·5 units from the observed numbers. The connection between the first subordinate series and the atomic mass is apparently simpler than between the other two series and the atomic mass.

The numbers in the last column were taken from Rydberg's paper.† He calculated them by means of an empirical formula, from the observed lines.

All the strong lines, and nearly all the weak lines which have been observed in the flame and arc spectra of these elements, are included in the three harmonic series of lines. The empirical formulæ given show that the differences in the corresponding series depend wholly on the atomic masses of the three elements.

* Author, *loc. cit.*

† 'Paris Congress Reports,' vol. 2, p. 212, 1900.